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Sorption of plutonium onto clinoptilolite (zeolite) colloids

N.L. Hakem, A. Brachmann, M. Zavarin and A. B. Kersting

Introduction:

Colloids may play a major role in the migration of radionuclides e.g., plutonium from nuclear waste disposed in a geologic repository [1]. Recent work by Kersting et al. (1999), detected plutonium 1.3 km from an underground nuclear test at Nevada Test Site (NTS) from which it was originally deposited [2]. The plutonium was associated with colloids that may enhance the transport of plutonium in the groundwater. These colloids consisted mainly of zeolite (mordenite, clinoptilolite/heulandite), clays (illite, smectite) and cristobalite (SiO_2).

The Environmental Protection Agency (EPA) found that plutonium deposited near Maxey Flats, Kentucky, had migrated hundreds of feet in less than 10 years [3]. In addition, plutonium was also detected in groundwater from test wells in West Valley, New York, suggesting that the plutonium had moved more than 50 feet in less than 25 years [4]. These field observations raise a number of questions regarding the dominant mechanisms that may control the plutonium migration. Kersting et al. (1999) suggested that the plutonium might sorb to colloids (zeolites or clays). In order to test this hypothesis, it is important to understand the effect of plutonium sorption and desorption onto the existing colloids found in NTS groundwater.

In the present work, we have performed a series of laboratory batch sorption experiments of plutonium (IV) on zeolite (clinoptilolite) colloids to understand the role of colloids in

the transport of plutonium under groundwater conditions similar to those found at the NTS.

Experiments:

Laboratory batch experiments were carried out at room temperature to evaluate the effect of time, plutonium concentration and pH on the sorption of Pu(IV) onto clinoptilolite colloids.

Water samples were collected from a well (WW-20) located on the NTS that has water representative of the water hosted in the volcanic aquifers at the NTS. The samples were filtered prior to use. The chemical analysis of the water indicated the presence of HCO_3 (110 ppm), Na (60 ppm), SO_4 (32 ppm) and Si (21.9 ppm), the pH and the conductivity were 7.96 and 296 μS/cm, respectively.

Colloid particles were prepared in WW-20 water by grinding a pure amount of clinoptilolite. Final concentration and particles size were 0.3mg/ml and of 90 ± 10 nm, respectively. Plutonium (IV) concentration was $5x10^{-9}$ M.

The zeta potential and the size variations of the colloids were measured as a function of pH by Electrophoretic Light Scattering and Photon correlation Spectroscopy (PCS), respectively.

Results:

The zeta potential of the colloids was always negative for pH ranging between 2.7 and 10.5. This negative charge is assigned to the progressive deprotonation of the surface of the colloids as the pH increased. The size of the particles increased at the lower pH range, from the original 90 nm of the starting material to approximately 342 nm indicating a partial coagulation of the colloids at low pH where their surface charge is minimum.

Using the software Mineql^{+}, we determined the speciation of plutonium Pu(IV) in WW-20 water as a function of pH. $Pu(CO_3)^{4-}{}_4$ and $Pu(CO_3)^{6-}{}_5$ are the dominant species around pH 8.

At the WW-20 water pH (8), the clinoptilolite colloids have a negative charge, a size of 90 nm and Pu(IV) is highly carbonated.

A kinetic study showed that the Pu(IV) sorption reached the equilibrium after 4 days. It was found that the sorption was dependent of the pH variation, e.g., the sorption ratio increased from 30% to 90% as the pH increased from 2.4 to 11.8 for a concentration of Pu(IV) equal to $5x10^{-9}$ M.

We are presently fitting the sorption data to several surface complexation models using the FITEQL code [5]. Initial data fits indicate that the sorption is comparable to Pu(IV) sorption to smectite reported by Sanchez [6].

Acknowledgements

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